

WATER-RESISTANT TELECOMMUNICATION CABLE**Field of the invention**

The present invention relates to telecommunication cables, in particular optical fiber cables, comprising elongated elements, in particular buffer tubes, which are capable of blocking a flow of water accidentally penetrated therein.

Background art

International patent application WO 00/21098, in the name of the same Applicant and herein incorporated by reference, discloses elongated solid elements housing at least one optical fiber therein, said elements being made from a water soluble material which, upon being contacted by water, dissolves at least in part and forms a viscous solution of suitable viscosity capable of stopping the longitudinal flow of water along said element. The use of buffer tubes of this kind allows to avoid the use, or at least substantially reduce the amount, of conventional water-blocking means, such as grease-like material, water-swellaable powders and the like.

In particular, said element is preferably a buffer tube and is preferably made from a vinyl alcohol/vinyl acetate copolymer (VA-VAc copolymer), generally identified in the art as polyvinylalcohol. These copolymers are generally obtained from partial or complete hydrolysis (i.e. saponification) of the acetate groups of a polyvinyl acetate polymer. Thus, these materials are generally identified by their hydrolysis (or saponification) degree, i.e. the percentage of acetate groups which has been hydrolyzed from the initial vinylacetate polymer. Typically, VA-VAc copolymer having a hydrolysis degree of 98% or higher are considered substantially completely hydrolyzed (or saponified), and are thus referred to as substantially completely hydrolyzed (or saponified) polyvinylalcohol.

As mentioned in WO 00/21098, the water-blocking capacity of the VA-VAc copolymer depends, among other properties, also from the degree of hydrolysis of the material. In particular VA-VAc copolymers completely hydrolyzed are almost insoluble in water, thus being substantially prevented from forming the desired water-blocking viscous solution. Accordingly, WO 00/21098 suggests to employ VA-VAc copolymers

having a hydrolysis degree of from about 50% to 95%, preferably from 70% to about 90%.

The Applicant has now observed that, while a buffer tube made from said VA-VAc copolymer solves the problem of effectively stopping a flow
5 of water accidentally penetrated inside the cable, its water blocking properties may be impaired upon aging.

In particular the Applicant has observed that, as a consequence of the aging of the material, the water blocking properties of the material can be impaired due to hydrolysis of the acetic groups of the copolymer. In
10 particular, the degree of hydrolysis of the VA-VAc copolymer may increase to such an extent as to severely limit the water blocking properties of the material.

In the art it is known to add compounds (e.g. antioxidants and/or thermal stabilizers) to polymeric compositions, to avoid oxidation and
15 thermal degradation which may occur, for instance, at the high temperatures during the processing of the material, e.g. during the extrusion process. These additives are however generally employed in very limited amounts. For instance, European patent EP 0 458 509 discloses oxidation resistant ethylene/vinyl-alcohol copolymer
20 compositions, having a saponification degree higher than 90%, preferably higher than 95% and comprising 0.01% to 0.5% w/w of a hindered phenolic antioxidant.

The Applicant has now found that the negative aging phenomena of a VA-VAc copolymer can be avoided or at least substantially reduced by
25 adding to said copolymer an effective amount of a hydrolysis stabilizer compound having a specific chelant structure, capable of chelating those site on the VA-VAc copolymer chain which are deemed responsible for the hydrolysis phenomena upon aging.

Summary of the invention

30 A first aspect of the present invention thus relates to a telecommunication cable, in particular an optical fiber cable, comprising an elongated element housing at least one transmitting element, said elongated element comprising a water-soluble polymeric composition which comprises:

- a vinyl alcohol/vinyl acetate copolymer having a saponification degree of from about 60% to about 95%;
 - a plasticizer;
 - a hydrolysis stabilizer compound comprising a chelant group
- 5 comprising two hydrogen atoms bonded to two respective heteroatoms selected from nitrogen, oxygen and sulphur?, said two hydrogen atoms having a distance between each other of from 4.2×10^{-10} m to 5.8×10^{-10} m, preferably of from 4.5×10^{-10} m to 5.5×10^{-10} m, said stabilizer compound being present in an amount of at least 0.75
- 10 mmoles per 100 g of VA-VAc copolymer.

Preferably the amount of said chelant group is of at least 0.8 mmoles, more preferably of at least 1.0 mmoles, per 100 g of VA-VAc copolymer. Said amount is preferably lower than about 3.5 mmoles, more preferably lower than about 3.0 mmoles, of chelant group per 100 g of VA-VAc

15 copolymer.

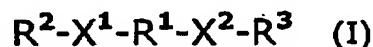
Preferably, said two heteroatoms forming said chelant group are nitrogen atoms. More preferably, said two nitrogen atoms are included in two respective amide moieties of formula $-\text{CO}-\text{NH}-$.

The amount of VA-VAc copolymer is preferably from about 50% to

20 about 95% of the total weight of the polymeric composition, more preferably from about 60% to 85.

Preferably said plasticizer is present in an amount of from 5 to 30 parts by weight per hundred parts by weight of the VA-VAc copolymer, more preferably from 10 to 25 parts.

25 Said stabilizer compound is preferably a compound of formula I:



wherein

R^1 represents a linear or branched C_1 - C_{10} alkylene, optionally substituted with one or two groups selected from alkyl substituted or

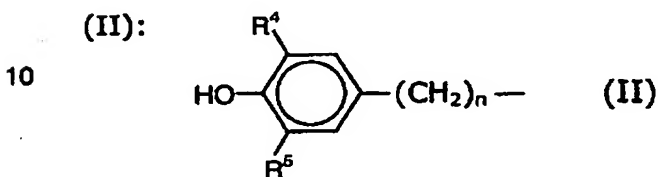
30 unsubstituted phenyl, benzyl or hydroxyphenyl;

X^1 and X^2 each independently represent a moiety comprising a heteroatom-bonded hydrogen selected from $-\text{NH}-$, $-\text{CO}-\text{NH}-$, $-\text{CH}(\text{OH})-$ or $-\text{CH}(\text{SH})-$;

each of R^2 and R^3 independently represent a linear or branched C_1 - C_{10} alkyl, optionally substituted with a group selected from alkyl substituted or unsubstituted phenyl, benzyl or hydroxyphenyl.

In particular, the combination of groups R^1 , R^2 and R^3 is selected in order to determine energetically feasible conformations of the molecule, wherein the distance between the heteroatom-bonded hydrogen atoms of X^1 and X^2 is as above identified.

Preferably R^2 and R^3 each independently represent a moiety of formula (II):



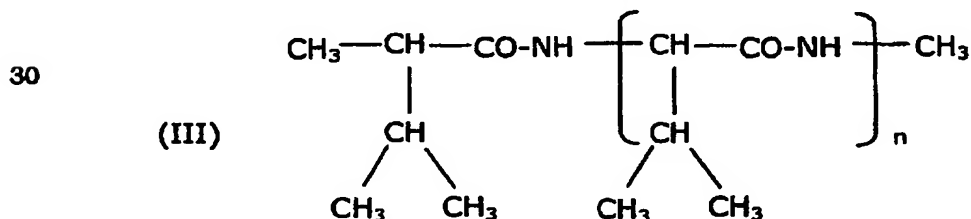
wherein R^4 and R^5 independently represent a C_1 - C_6 linear or branched alkyl moiety, preferably t-butyl, and n is an integer from 0 to 6, preferably 2.

Preferably R^1 is a linear C_2 - C_{10} alkylene, more preferably a C_6 alkylene.

Preferably said heteroatom moieties X_1 and X_2 are amide groups of formula $-CO-NH-$.

According to a particularly preferred embodiment, said stabilizer compound is N,N'-esan-1,6-dilblis[3,5-di-ter-butyl-4-hydroxyphenyl)proplonamide].

Alternatively, said stabilizer compound can be an oligomer or polymer formed by a plurality of monomeric units, each of said monomeric unit comprising at least one heteroatom-bonded hydrogen atom, wherein the energetically feasible conformations of the molecule provide a distance between two of said heteroatom-bonded hydrogen atoms of two respective monomeric units as above identified. For instance, said stabilizer compound can be a poli L-aminoacid of formula (III):



where n is an integer from 1 to 5.

Preferably said VA-VAc copolymer has a hydrolysis degree of from about 70% to about 92%, more preferably from about 70% to about 90%.

According to a preferred embodiment, said elongated element
5 containing the at least one optical fiber is a tubular element comprising at least one sheath made from said water-soluble polymeric composition.

Preferably, said tubular element comprises a double layer sheath in which the inner sheath is made from said water-soluble polymeric composition and the outer sheath is made from a conventional water-
10 insoluble polymer material, preferably polyethylene.

According to a further preferred embodiment, the said tubular element comprises a third outer sheath made of water-soluble polymeric composition as above defined.

According to an alternative embodiment, said elongated element is a
15 grooved core comprising at least one groove longitudinally disposed on the outer surface of said core and housing said at least one optical fiber. According to an embodiment of the present invention, at least the walls of said groove are made from a water-soluble solid polymer composition. According to an alternative embodiment, said grooved core is made
20 completely from said water-soluble solid polymer composition.

According to another alternative embodiment, the element made of water-soluble solid material included in a cable according to the present invention is a tape.

For the purpose of the present invention, the term "transmitting
25 element" includes within its meaning any element capable of transmitting a signal, particularly optical fibers, including individual optical fibers, ribbons or bundles of optical fibers, either as such or protected by a polymeric sheath. Non limiting examples of optical fibers are, for example, single-mode fibers, multi-mode fibers, dispersion-shifted (DS)
30 fibers, non-zero dispersion (NZD) fibers, or fibers with a large effective area and the like, depending on the application requirements of the cable. They are generally fibers with an outside diameter of between 230 and 270 μm .

Brief description of the drawings

Fig. 1 shows a cross-sectional view of an elongated element for a cable according to the invention.

Fig. 2 shows a cross-sectional view of an alternative elongated element for a cable according to the invention.

Fig. 3 shows a cross-sectional view of an cable according to the invention.

Fig. 4 shows a cross-sectional view of an alternative embodiment of a cable according to the invention.

Description of preferred embodiments

Fig. 1 shows an example of an elongated element comprised in a cable according to the invention. In this embodiment, said element is a tubular element in particular a buffer tube **10**, which comprises a polymeric sheath **11** which envelopes a plurality of transmitting elements **12**. The polymeric sheath **11** is made from a water-soluble polymeric material as above defined. Transmitting elements are preferably optical fibers which can be disposed inside the tube either individually, as ribbons or grouped into bundles. Bundles of optical fibers (e.g. twelve) may also be semi-tightly enveloped by a so-called microsheath, i.e. a sheath of polymeric material (e.g. ethylene-propylene copolymer) having a thickness of about 0.15 mm, to form microtubes which are disposed within buffer tube **10**. If desired, said microtubes may contain waterblocking means, in the form of grease like filler or preferably in the form of water swellable powder compositions. For instance a composition comprising a mixture of polyacrylate water swellable particles and inert talc particles, as described in International Patent Application WO 00/58768, herein incorporated by reference, can be used. If desired, some of the optical fibers housed inside said buffer tube can be replaced by non-transmitting glass fibers, in order to reach the optimal count within the tube, without varying the dimensions of the tube.

Figure 2 shows a preferred embodiment of an elongated element comprised in a cable according to the invention. Buffer tube **20** comprises a double layer sheath, where the outermost sheath **21** is made from a conventional polymer material. Conventional polymer materials

are, for instance polyethylene, ethylene-propylene copolymers, polypropylene or polybutyleneterephthalate. Preferably polyethylene, in particular high density polyethylene, is employed. The innermost sheath **22**, enveloping a plurality of transmitting elements **12** as above defined, is made from a solid water-soluble polymer composition as described above. A buffer tube **20** can be manufactured according to conventional extrusion techniques for manufacturing double-layer sheaths, such as, for instance, co-extrusion.

The internal diameter of buffer tubes **10** or **20** is preferably from about 1.5 mm to about 2.0. The thickness of the sheath comprising the water-soluble polymer composition is preferably from about 0.2 to about 0.3 mm. The thickness of the outer polymeric layer **21** is preferably from about 0.2 to about 0.4 mm

Figure 3 shows an example of a cable according to the invention, comprising a supporting element **30**, preferably made from a central reinforcing element, typically made of glass resin, coated with a layer of polymer, e.g. polyethylene.

The cable has one or more buffer tubes **31**, wound around the supporting element **30**. The buffer tubes are like those illustrated in figure 1 or preferably in figure 2. Where appropriate, buffer tubes **31** may further comprise an outer layer comprising the water-blocking material.

The number of buffer tubes (which may also be arranged on several layers) and their dimensions depend on the intended capacity of the cable, as well as on the conditions of use of this cable.

For example, cables are envisaged with only one tubular element (in which case the central element **30** is not present), and cables are envisaged with six, eight or more buffer tubes, wound in one or more layers (for example up to 24 tubular elements bundled on two layers).

The buffer tubes **31** are in turn held together by a containing layer **32**, for example a wrapped polymeric tape, and are preferably surrounded by a reinforcing element **33**, for example a layer of Kevlar® fibres or of glass yarn, the size of which depends on the mechanical strength requirements of the cable. If desired, the containing layer **32** can be made (entirely or partly) by wrapping with a tape of water-blocking

polymer composition as above defined, or alternatively with an extruded layer of the same composition.

Two sheath-dividing filaments **34**, arranged longitudinally with respect to the cable, can be included within the reinforcing layer **33**.

- 5 The cable then comprises a protective outer sheath **35**, typically made of polyethylene, preferably medium density polyethylene. In relation to specific requirements, further protective layers can also be present, for example of metal layers, either inside or outside the structure described.

- Figure 4 shows another embodiment of a cable according to the
10 invention, of the slotted core type. Said cable comprises, in its radially innermost position, a reinforcing element **40** made, for example, of glass resin, on which is present a grooved (or slotted) core **41** (which is typically extruded on the reinforcing element), made of water-soluble polymer composition according to the invention. The grooves **42** extend
15 in a continuous helix or in an alternating s-z path all the way along the entire outer surface of the said core, in order to house the optical fibres **43** therein; in a similar manner to that mentioned above, the optical fibres can be arranged individually or assembled in ribbons, mini-tubes and the like, loosely (i.e. with an excess of length) or tightly at the
20 bottom of the grooves.

- According to an alternative embodiment, said grooved core can be made only in part from the water-soluble polymer composition. In this case, a double layer grooved core is manufactured (e.g. by double-extrusion or co-extrusion of the two polymer layers), wherein the inner
25 portion of the core is made from a conventional polymer material (e.g. PE or PP) and the outer grooved portion is made from a water soluble polymer composition according to the invention.

- Alternatively, the grooved core can be made entirely from a conventional material, such as PE or PP. In this case, U-shaped elongated
30 elements made of water-soluble composition can be placed in its grooves, it being possible, for example, for these elements to be co-extruded with the grooved core or produced separately and subsequently inserted into the grooves.

As an example, the grooved core can be between 4 and 12 mm in diameter and can comprise from 1 to 10 grooves, depending on the capacity of the desired cable. The dimensions of the grooves themselves are determined by the number of fibres present therein (which may be assembled as tapes of fibres) and by the degree of freedom envisaged for these fibres.

The grooved core **41** is then coated with a layer **44** of polymer, preferably comprising said water-soluble composition, which closes off the grooves; this coating can be made either in the form of an extruded sheath or as a longitudinal or helical wrapping.

This layer can in turn be surrounded by a further reinforcing tape **45** made, for example, of polyester, and is then surrounded by a reinforcing layer **46** or armouring made, for example, of Kevlar®, which can incorporate filaments or rods made of solid, water-soluble composition.

A further wrapping **47** made, for example, of polyester surrounds the armouring **46** and is in turn encircled by an outer sheath **48** typically made of polyethylene, particularly MDPE; a layer of water-soluble polymer composition **49** can be placed under the outer sheath **48**, e.g. as a wrapped tape or as extruded sheath, and in all of the zones which can conceivably be reached by water.

The VA-VAc copolymer comprised in an elongated element according to the invention, is preferably selected among those having a degree of hydrolysis of from about 60% to about 95%, more preferably from about 70% to about 92%, much more preferably from about 70% to about 90%.

Furthermore, it is also preferable to use a vinyl alcohol/vinyl acetate copolymers with a viscosity index of greater than about 10. Preferably, the viscosity index of the copolymer is between about 12 and about 40, vinyl alcohol/vinyl acetate copolymers with a viscosity index of between about 15 and about 35 being particularly preferred. Advantageously, it is possible to use mixtures of copolymers with different viscosity indexes (i.e. different molecular weights), so as to combine the specific advantageous effects of each copolymer.

Examples of commercially available materials with the desired properties are those sold under the trade name Mowiol® (Hoechst AG), Gohsenol® (Nippon Gohsei), Elvanol® (Du Pont) or Airvol® (Air Products).

- 5 The amount of VA-VAc copolymer in the polymeric composition forming said elongated element is preferably from about 50% to about 95% of the total weight of the polymeric composition, more preferably from about 60% to 85.

As previously mentioned, the Applicant has found that a VA-VAc
10 copolymer forming an elongated element according to the invention can be protected against the aging effects caused by hydrolysis phenomena, by adding an effective amount of a hydrolysis stabilizer compound comprising at least two hydrogen atoms bonded to two respective heteroatoms selected from nitrogen, oxygen and sulphur, said at least
15 two hydrogen atoms having a distance of from 4.2×10^{-10} m to 5.8×10^{-10} m, preferably of from 4.5×10^{-10} m to 5.5×10^{-10} m.

Although not willing to be bound to any particular theory, the Applicant is of the opinion that a compound with the above features is capable of effectively interacting with the polymeric chain of the VA-VAc copolymer
20 in order to limit the hydrolysis of the residual acetate groups.

In particular, the distance between said hydrogen atoms in the energetically feasible conformations (particularly in the lowest energy conformation) of the molecule of the stabilizer compound, should be capable of forming hydrogen bonds with two respective oxygen atoms of
25 the VA-VAc copolymer having a distance between about 4.5×10^{-10} m to 5.5×10^{-10} m.

As previously mentioned, the VA-VAc copolymer is generally obtained by hydrolysis of polyvinylacetate, by which the acetate groups of the polymer are converted to hydroxy groups. More specifically, the reaction
30 is typically an alcoholysis of polyvinylacetate with a metal (typically sodium) hydroxide as catalyst. The VA-VAc copolymer resulting from the alkaline alcoholysis has mainly a block structure, where blocks formed by sequences of vinyl-acetate groups of formula $-\text{CH}_2-\text{CH}(\text{OCOCH}_3)-$ are

alternated to blocks formed by sequences of vinyl-alcohol groups of formula $-\text{CH}_2-\text{CH}(\text{OH})-$.

As observed by the Applicant, upon aging and in presence of humidity, the hydrolysis reaction on a partially hydrolyzed VA-VAc copolymer tends to continue with consequent formation of acetic acid, which in turn acts as a catalyst of the hydrolysis reaction. Due to the block structure of the VA-VAc copolymer, the Applicant is of the opinion that the acetate groups which are more prone to the hydrolysis attack (i.e. which require less activation energy) are those of the terminal vinylacetate moieties of each vinylacetate block.

The Applicant has then determined by means of structural analysis, that the interatomic distances between the different oxygen atoms of the acetate and hydroxy groups at the interface of the respective block-terminal vinylacetate and vinylalcohol groups are comprised between 4.5 and 5.4 Angstrom (10^{-10} m) in the most probable energetically feasible conformations of the VA-VAc copolymer.

As experimentally determined by the Applicant, a chelant molecule having two heteroatom-bonded hydrogen atoms at a suitable distance, i.e. comparable with those determined between the above mentioned oxygen atoms of the VA-VAc copolymer, is capable of effectively preventing the hydrolysis attack on the VA-VAc copolymer chain. It is in fact believed that these two heteroatom-bonded hydrogen atoms are capable of forming hydrogen bonds with respective oxygen atoms on the VA-VAc copolymer chain, thus creating a chelated structure at the interface between a vinylacetate and a vinylalcohol block, which effectively protects the acetate group from hydrolytic attack.

As a matter of fact, other compounds generally employed as antioxidants, which do not however show the above interatomic distance between two heteroatom-bonded hydrogen, do not explicate the desired aging-protective effect against hydrolysis of the acetate groups.

Determining the distance between atoms is within the skill in the art. For instance, software with which such determinations are optionally made includes CAChe software commercially available from CAChe Scientific, Inc.; PCMODEL software commercially available from Serena

Software; HSC Chemistry for Windows, or PCMODEL software commercially available from AR Software; INSIGHT II, DISCOVER, and LUDI software commercially available from BIOSYM; SYBYL, RECEPTOR, and DISCO software commercially available from Tripos Associates, Inc.;
5 and New Chem-X commercially available from Chemical Design, Inc. Examples of such modeling include those disclosed in U.S. Pat. Nos. 5,187,086; 5,250,665; 4,859,769; 5,208,152; 4,980,462; 5,202,317; 5,196,404; 4,781,977, and 5,175,273. Alternatively, X-ray crystallography data can be used to ascertain distances. The
10 crystallography data is preferably input to a programmed computer or microprocessor to determine distances. Alternatively, molecular models can be used to determine interatomic distances when the models are dimensionally correct. Examples of such modeling include those disclosed in U.S. Pat. Nos. 4,877,406; 4,906,122; 4,622,014, and 5,030,103.
15 Because of speed and accuracy, determining distances using a programmed computer or microprocessor is preferred.

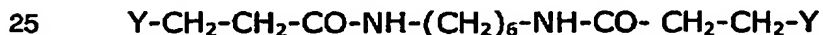
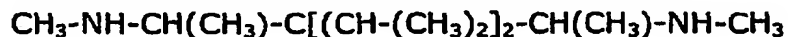
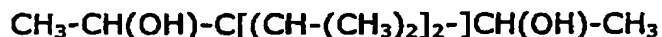
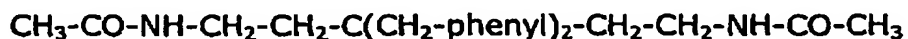
It is within the skill in the art that such distances are determined at energetically feasible conformations, preferably the lowest energy conformation. An energetically feasible conformation is a conformation
20 having a heat of formation within about 1.5 KCal (6285 Joule (J)) of the heat of formation of the lowest energy conformation. Ascertaining the lowest conformation in the energetically feasible conformation is within the skill in the art as shown by such references as Reviews in Computational Chemistry II, Lickowitz et al. ed., VCH Publishers, 1991, pp. 1-47 and Hehre et al., Experiments in Computational Organic
25 Chemistry, Wavefunction, Inc., 1993, pp. 47-66. Software is advantageously used in calculating these conformations. Software is also advantageous in calculating heats of formation of each conformation and the distances between atoms. The lowest energy conformation and
30 energetically feasible conformations are preferably determined by means known as (a) semiclassical (model), harmonic, or molecular mechanical; (b) semiempirical quantum mechanical; and/or (c) ab initio quantum mechanical methods.

These methods are within the skill in the art as shown by Reviews in Computational Chemistry II, Lickowitz et al. ed., VCH Publishers, 1991, pp. 313-315.

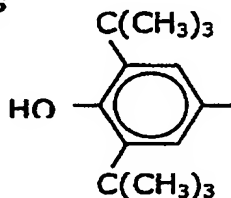
It is also within the skilled in the art (see e.g the article from R. Scordamaglia and L. Barino "Theoretical predictive evaluation of new donor classe in Ziegler-Natta heterogeneous catalysis for propene specific polymerization", Macromol. Theory simul., 7, 399-405, 1998) the use of statistical methods applied to the molecular modelling analysis, for assigning probabilistic weights to each of the determined energetically feasible conformations. Upon identification of a specific molecular parameter (such as the interatomic distance between two atoms of the molecule, as in this case), it is then possible to calculate the probability of a selected value (or range of values) of said parameter being present in said molecule, as the sum of each probability assigned to the respective energetically feasible conformations showing said selected value of said parameter.

Preferred hydrolysis stabilizer compounds are those of formula (I) previously indicated, showing the above distance between the two heteroatom-bonded hydrogen atoms.

Examples of suitable compounds falling within the compounds defined by formula I are the following:

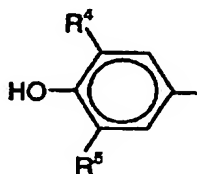


where Y is



Among those compounds of formula I, particularly preferred are those comprising at least one and preferably two hindered phenols, i.e. a pheno, group with sterically bulky substituents located ortho to the OH moiety. Said hindered phenols are preferably comprised in the R² and R³

substituents of the compound of formula I. Examples of suitable hindered phenols are those of formula:



wherein R⁴ and R⁵ independently represent a C₁-C₆ linear or branched alkyl moiety, preferably t-butyl.

The presence of the hindered phenols in the stabilizer compound may contribute to the confer (additional) thermal and oxidative stability to the polymeric mixture during processing of the material.

Further preferred compounds are those compounds of formula I wherein the X₁ and X₂ moieties are -CO-NH- group.

A particularly preferred stabilizer compound is N,N'-esan-1,6-dilbis[3,5-di-ter-butyl-4-hydroxyphenyl]propionamide].

An example of a suitable commercially available material is Irganox 1098 (Ciba Geigy).

As the effect of the stabilizer depends from the chelant group formed by the two heteroatom-bonded hydrogen atoms, it is convenient to express the amount of stabilizer to be added to the VA-VAc copolymer as the millimoles of chelant groups for 100 grams of VA-VAc copolymer. In case of a molecule of stabilizer bearing a single chelant group (such as those compounds of formula I), the millimoles of chelant groups correspond to the millimoles of compound. As observed by the applicant, an amount of stbllizer of at least 0.75 mmoles per 100 g of VA-VAc copolymer, preferably of at least 0.8 mmoles, is advantageous to achieve an effective stabiliztion of the VA-VAc copolymer. Much more preferably, said amount is of at least 1.0 mmoles of chelant groups per 100 g of VA-VAc copolymer.

The Applicant has further observed that while the amount of the hydrolysis stabilizer should be sufficiently high for resulting in the desired stabilizing effect, it is however advisable to avoid excessive amounts of this additives, thus keeping said amount below the above indicated maximum amount. As a matter of fact, excessive amounts of stabilizer, particularly when the heteroatom groups X₁ and X₂ are amine groups,

may cause undesirable cross-linking reactions in the VA-VAc copolymer, with consequent difficulties in processing the material. The amount of stabilizer should thus preferably be lower than about 3.5 mmoles of chelant groups per 100 g of VA-VAc copolymer, more preferably lower than about 3.0 mmoles.

For instance, the Applicant has found that if N,N'-esan-1,6-diilbis[3,5-di-ter-butyl-4-hydroxyphenyl)propionamide] (Irganox 1098, Ciba Geigy) is used as stabilizer compound, it is preferable to use from about 0.78 to about 3.2 mmoles of compound (which comprises a single chelant group) per 100 g of VA-VAc copolymer. This amount corresponds to an amount from about 0.5% to about 2.0% by weight with respect to the total weight of VA-VAc copolymer (0.5 to 2.0 phr).

Further to the excessive amount of stabilizer, undesirable cross-linking of the VA-VAc copolymer can also take place during the mixing of the VA-VAc copolymer with the stabilizer compound, if too much energy (heat or mechanical) is transferred to the polymer during the mixing. The stabilizer should thus preferably be admixed by controlling the energy transfer, e.g. as indicated in US patent 5,137,969, herein incorporated by reference. Preferably a co-rotating twin screw extruder is used.

The addition of a stabilizer compound as above defined allows thus to reduce the negative effects of aging on the VA-VAc copolymer, in particular by reducing the hydrolysis phenomena of the acetate groups. The reduction of the hydrolysis phenomena determines in fact a reduced increase in the hydrolysis degree of the material, which may thus perform its water-blocking function also after aging.

In the practice, a VA-VAc copolymer is commonly identified by means of its saponification number, which corresponds to the mg of KOH which are necessary to hydrolyzed one gram of VA-VAc copolymer. The hydrolysis degree (HD) is correlated to the saponification number (SN) of the VA-VAc copolymer through the following formula:

$$HD = 100 \cdot \frac{100 - 0.1535 \cdot SN}{100 - 0.0749 \cdot SN}$$

where the hydrolysis degree is expressed as the mole % of hydrolyzed vinylacetate groups.

On polymeric compositions comprising a VA-VAc copolymer, it is generally easier to measure the saponification number of the whole composition (i.e. on the whole weight of the composition), which will thus be lower than the saponification number of the only VA-VAc copolymer comprised in the composition. If necessary, by knowing the weight percentage of VA-VAc copolymer in the compositions, it is possible to calculate the saponification number of the VA-VAc copolymer and then, according the above formula, the respective hydrolysis degree.

The polymeric mixture may further comprise conventional additives such as plasticizers, oxidation/thermal stabilizers, biocides, processing aids, pigments and the like.

The amount of plasticizer is preferably from about 5% to about 30% by weight with respect to the weight of VA-VAc copolymer, more preferably from about 10% to about 25%.

Examples of suitable materials which can be used as plasticizers are glycerol, sorbitol, trimethylolpropane, low molecular weight polyglycol, such as polyethylene glycol (e.g. di- or tri-ethyleneglycol), pentaerythritol, neopentylglycol, triethanolamine or oxyethylated phosphoric esters.

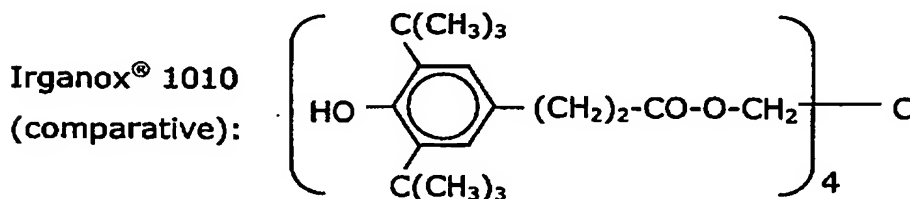
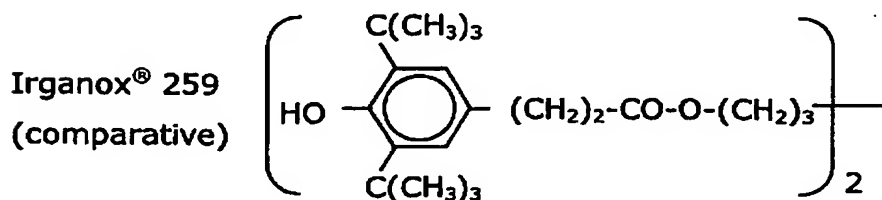
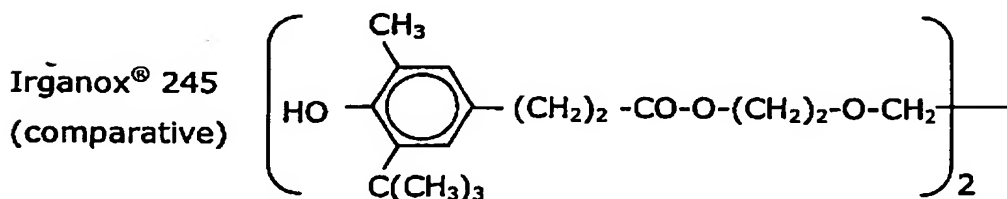
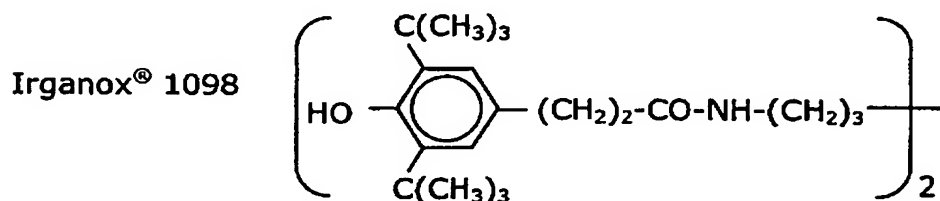
Whilst the hydrolysis stabilizer of the present invention may include in the preferred embodiment a hindered phenolic group capable of limiting the oxidation phenomena and thermal degradation which may occur at the high temperatures during the processing of the material, nevertheless it may be advantageous to add to the polymeric mixture small amounts of an oxidation/thermal stabilizer, e.g. in an amount of from about 0.05 to about 0.5. Examples of suitable oxidation/thermal stabilizer are hindered phenolic antioxidants, such as those commercialized under the tradename Irganox by Ciba.

The following non-limitative examples are given for better illustrating the invention.

EXAMPLES**Example 1****Preparation of VA-VAc copolymer compositions**

The hydrolysis stabilizing effect of different additives and different amounts of said additives has been verified on a polyvinylalcohol composition comprising a Mowiol 26/88 (Clariant) as VA-VAc copolymer and 25 phr of glycerol as plasticizer, extruded in a conventional manner to form buffer tubes.

The following additives of the hindered phenolic type have been used:



Four polymeric compositions have been prepared by adding an amount of 1 phr of the above additives to the initial VA-VAc copolymer composition (i.e. 1 part of additive per 100 part by weight of VA-VAc

copolymer). For Irganox 1098, this amount corresponds to 1.57 mmoles of compound per 100 g of VA-VAc copolymer.

Two further comparative composition have been prepared by mixing and granulating as above the initial VA-VAc copolymer composition, but
5 adding to the VA-VAc copolymer and plasticizer:

- 0.1 phr of Irganox 245; or
- 0.1 phr of Irganox 245 and 0.32 phr of EMBAC (corresponding to 1,57 mmoles per 100 g of VA-VAc copolymer);

where EMBAC is the acronym indicating hexamethylenbisacetamide:
10 $\text{CH}_3\text{-CO-NH-(CH}_2\text{)}_6\text{-NH-CO-CH}_3$.

The six compositions are identified as follows:

Composition	Additive
1	Irganox 1098
2*	Irganox 245 (0.1 phr)
3*	Irganox 245
4*	Irganox 259
5*	Irganox 1010
6*	EMBAC + Irganox 245

*comparative

The composition have been prepared feeding a blend with a gravimetric feeder comprising 100 parts of Mowiol 26/88 and the additive into a 30
15 mm co-rotating twin screw extruder (35 L/D long , vent at the 25 diameter position) and injecting 25 parts of glycerol at the 8 diameter position. Operating conditions were as follows:

- screw speed: 100 rpm
- production rate: 10 kg/h
- 20 - melt temperature (at the exit from the extruder: 200°C
- specific energy input: 0.13 KW h/kg

The strands were cooled in air and granulated into pellets.

The pellets have been subsequently extruded in the form of e buffer tube (outside diameter 2.1 mm, thickness 0.25 mm) according to
25 conventional extrusion techniques.

The so obtained buffer tubes were tested for measuring the number of saponification according to the following procedure.

Specimens of tubes of a weight about 1.0 g have are previously treated under a flow of 280 NI/h of nitrogen for 1 h at the temperature of 180°C for removing possible amounts of free acetic acid. The number of saponification has been determined as follows.

The specimens so treated is accurately weighed on analytical weight, inserted into a 500 ml flask, added with 100 ml of distilled water, and the mixture is stirred under moderate heating up to dissolution of the specimen.

25.0 ml of 0.1 N potassium hydroxide solution are then added to the mixture, together with few drops of indicator, and the solution is stirred while heating to reflux for one hour.

A blank test is conducted in parallel, with the same amount of reactants, but without the polymeric material.

Titration is effected with a 0.1 N solution of sulfuric acid.

The saponification number (i.e. the grams of reacted potassium hydroxide per gram of polymeric material) is calculated as follows:

$$\text{Saponification No.} = 5.61(\text{PB}-\text{P})/\text{g}$$

where PB are the ml of sulfuric acid solution used in the blank test, P are the ml of sulfuric acid used for the test with the polymer and g are the grams of polymeric composition.

Table 1: Saponification number after extrusion

Composition	Saponification No.
1	112.9
2	112.3
3	113.1
4	109.6
5	112.1
6	108.6

As shown by the above table, no substantial variation in the saponification number of the different compositions is observed on the non-aged compositions.

EXAMPLE 2

Specimens of the buffer tubes obtained according to example 1 has then been subjected to accelerated aging, by introducing the specimens
5 into an oven under controlled relative humidity (50%) at a temperature of 85°C for 30 days.

At the end of the aging test, the saponification number of each specimen has been measured according to the methodology described in example 1. Table 2 shows the results of the measurement, with the
10 percentage variation of the saponification number with respect to the one of non-aged specimen reported in table 1.

Table 2: Saponification number after aging

Composition	Saponification number	% variation of saponification no.
1	105.7	6.3
2	96.7	13.9
3	97.9	13.4
4	96.1	12.3
5	95.5	14.8
6	94.4	13.1

From the above table, it can be appreciated that while other
15 conventional hindered phenolic antioxidants are not able to limit the increase of hydrolysis degree (i.e. the reduction of the saponification number) of the VA-VAc copolymer, an effective amount of a compound as illustrated in the foregoing of the present specification substantially limits the hydrolytic degradation of the polymer material.

20 Two further test have been performed by varying the amount of Irganox 1098 in a composition as previously illustrated. In particular, an amount of 0.5 phr (0.78 mmoles per 100 g of VA-VAc copolymer) and of 0.1 phr have been used. In the first case, the variation of the saponification number was of about 9.5%, while in the second case of
25 about 12.1%.